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SYNTHESIS AND CHARACTERIZATION OF ZnO NANOPARTICLES HAVING PRISM SHAPE BY A NOVEL GAS CONDENSATION PROCESS

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Abstract. The objective of this paper is to develop an innovative nanoparticles synthetic system that applies the theory of gas condensation in producing nanoparticles. This system is made up of vacuum system, temperature control system, cold trap system and nanoparticles automatic collection system. Under a vacuum environment, the system would use the energy produced by high frequency induction method to vaporize the pure zinc rod inside the crucible. During the vaporization process, He gas is filled in, so that the high-temperature vaporized metal can undergo momentum exchange with He gas and at the same time, induce the vaporized metal to run to the low-temperature cold trap. Upon reaching the wall of the cold condenser having extremely low temperature, the vaporized metal would instantly condense, forming nanoparticles. The chemical composition was verified using the electron spectroscopy for chemical analysis(ESCA). It is known from the experiment that, this nanoparticles synthetic system can produce good quality ZnO nanoparticles having a shape of hexagonal prism. The FE-SEM image shows that its average diameter is 20 nm, and the size is very consistent. This paper also investigates into the relevancy of the ZnO nanoparticles towards the change of the time of repose and particle size when it is placed inside the de-ionized water. Besides, the Zeta potential and average diameter of ZnO nanofluid are also measured under different pH conditions, so as to analyze the stability of ZnO nanofluid suspension. Moreover, in order to verify the practicability of the fabricated ZnO nanoparticles, the ZnO nanofluid is inspected by UV/Vis absorption spectrum and the result shows that ZnO nanoparticles carries absorption ability within the wavelength that ranges from 350 to 550 nm.

1. INTRODUCTION

At present, there are lots of methods in producing nanoparticle, and the commonest one is gas condensation method, which the development of this technology can be traced back to 1960's [1-4]. The synthesis technology is very sophisticate nowadays and in Japan, metal nanoparticle products that are produced by vacuum metallurgy have already been available in the market. These products are mainly applied to magnetic recording media material and thick film conductivity or photoresist powder [5].

The method of this fabrication is to heat the metals under the condition of inert-gas such as low-pressure argon and nitrogen. Upon vaporization, the metal will turn into smog and move upward along with the convection of the inert-gas to get close to the cooling tank (77K) that is filled with liquid nitrogen. During the process of getting close to the cooling tank, the original material vapor will

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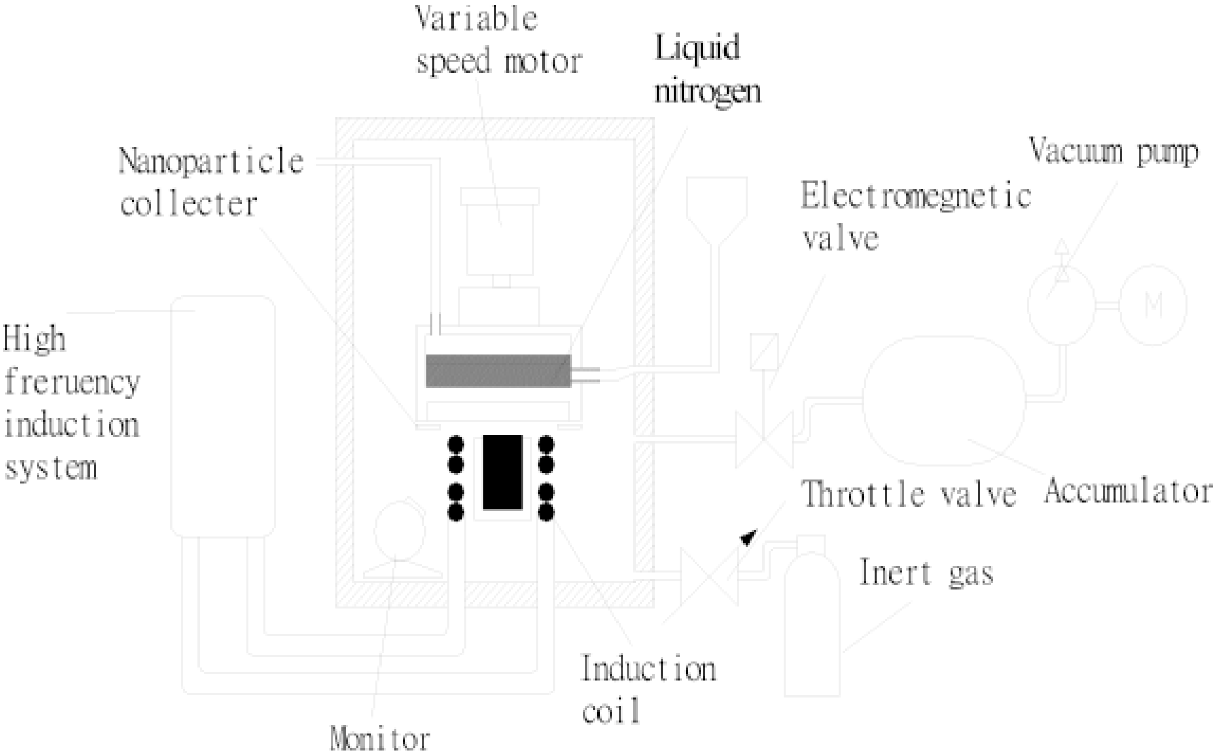


Fig. 1. Schematic diagram of the high frequency gas condensation fabrication system.

firstly form into atomic cluster, and then into single nanoparticle and finally aggregate on the surface of the cooling tank. Lastly, researcher can collect the powder of the nanoparticle by a scraper.

High frequency induction heating method is discovered in the early 1970's during the process of developing the production technology of nanoparticles for the use of high performance magnetic tape. This method is to heat the material inside the crucible by means of high frequency induction to fabricate nanoparticles. High frequency induction heating carries lots of merits in the application of vacuum molten metal, including 1. Stable temperature which can be maintained towards the metal solution that needs to be vaporized. 2. Alloy material inside the solution is well-balanced. 3. Steady production of nanoparticles and long-time operation. Points 1. and 2. are achieved by stirring the solution inside the crucible by the inductive stirring action, so that there is no temperature variance at the center and the rim of the vaporized surface, maintaining the balance of alloy inside the crucible.

ZnO is a metallic oxidized material which belongs to the Wurtzite structure having a symmetrical space group P63mc in the Hexagonal close-packed HCP. Its melting point is 1800 °C and since this structure is hexagonal and symmetrical, as well as not having a symmetrical center, so it carries the feature of high piezoelectricity. When it forms into ZnO single crystal under the environment of zinc and oxygen, phenomenon of the so-called metal redundant (or oxygen vacancies) along with zinc interstitials or oxygen vacancies occurs towards this single crystal, producing the n type semiconductor of displacement type that is applicable to luminescence device. Also, since ZnO has a high reflection rate (1.96~2.1) [6], it can perform optical penetration at the wavelength of 400~200 nm, demonstrating its characteristics of high photoelectric and non-linear optical coefficient. Also, ZnO has been applied in the production of gas sensor since it is easy to create the action of absorption with gas, generating change in the electricity [7-9].

Based on the basic theory of gas condensation method, this research develops an innovative nanoparticle synthesis system of which the main experimental equipment include: heating device, pressure balance system, automatic dry powder collection system. The heating system works in the form of induction heating, and the main function of pressure control system is to maintain the pressure inside the vacuum chamber, so that it can maintain the required pressure. In the aspect of parameter control, *A*/*D* conversion interface input controller is used, of which its interior can undergo preset temperature evaluation, so as to maintain a steady heating curve of the temperature of metallic vaporization. The powder produced by this processing is evenly distributed on the surface of automatic nanoparticle collector, and by means of automatic scraping equipment, the nanopowder can be massively produced.

The particle dimensions and morphology of the prepared ZnO nanoparticle was examined by field emission scanning electron microscope (FE-SEM). The chemical composition was verified using the electron spectroscopy for chemical analysis (ESCA). The zeta potential of the ZnO nanoparticle suspension was measured using zeta potential analyzer. Meanwhile, an Ultraviolet-Visible (UV-Vis) spectrophotometer was used to measure the optical property of the prepared ZnO nanofluids.

2. EXPERIMENTAL

Fig. 1 shows the schematic diagram of the experimental equipment of the nanoparticle fabrication system by means of high frequency gas condensation method that is developed in this research. It is mainly composed of high frequency induction heating system, temperature feedback system, vacuum pressure balanced system, real-time monitor system and nanoparticle collection system [10]. High frequency induction heating system can provide steady current to induce the material to heat, melt and vaporize into gas. Through the setting of high frequency current, temperature feedback system can capture the signal of thermal couple from the *AD/DA* card, so as to control the temperature inside the crucible and the speed of material vaporization. Vacuum pressure balanced system can maintain the vacuum pressure required for experiment inside the vacuum chamber. Real-time monitor system is built inside the vacuum chamber, which is mainly composed of components such as USB transmission line, special designed USB vacuum converter, USB white light bulb, and CCD monitor. Researchers can clearly monitor the full action inside the vacuum chamber and the metallic vaporization process by computer, which is referential to the timing of activating of the automatic collection system and observing the action of each component inside the vacuum chamber. Automatic nanoparticle collection system is placed in the vacuum system, which acts as segregating system together with the vacuum system. The liquid nitrogen is induced into the low-temperature storage tank, and inside the cooling collector, nitrogen becomes nitrogen gas upon heat absorption and vaporization, which is then induced out via pressure release opening. Nanoparticle collection system is composed by transformer device, DC motor, and pressure adjustable and rotational powder scraper mechanism. When the metal material reaches the vaporizing state, the condition of powder accumulating on the surface of the collector can be observed by means of real-time monitor system. And the automatic scraping system can be activated outside the vacuum chamber, effectively storing the nanoparticles on the scraper collection tank and collector.

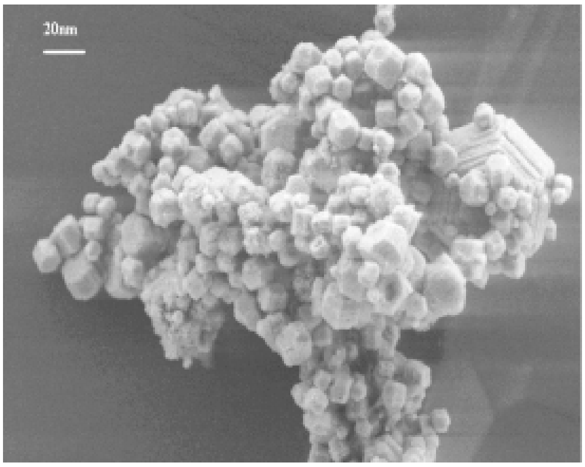
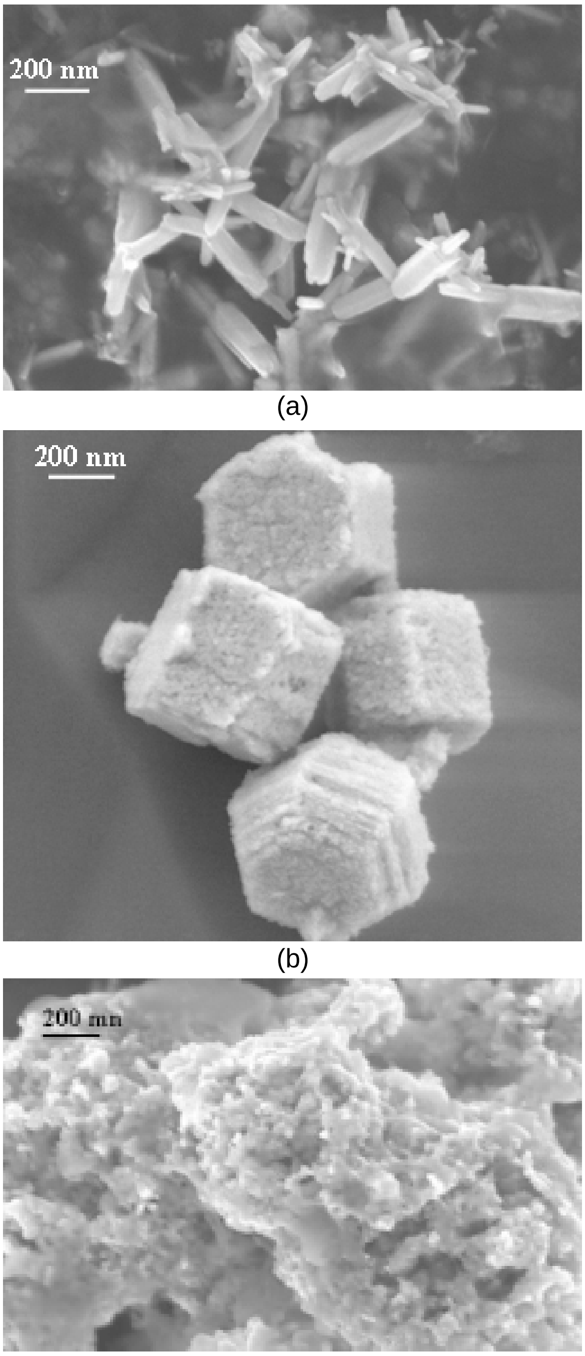


Fig. 2. FE-SEM image of ZnO nanoparticle produced by the automatic collector in the proposed system.

The metal bulk that needs to be generated into nanoparticles is placed into the crucible inside the vacuum chamber. Upon setting heating current, vacuum pressure and vaporized temperature, metal bulk will be heated due to the induced current, so that it will melt and vaporize into gas. Inside the vacuum chamber, the material vapor being vaporized will collide with the inert-gas and cool off, which then flow to the surface of the low-temperature collector and form into nanoparticles. Since the liquid nitrogen will continuously flow into the collector inside the vacuum chamber, the temperature of the surface of the collector should be



(a)

(b)

(c)

Fig. 3. FE-SEM image of ZnO nanoparticle that is placed in deionized water for (a) 72 h (b) 168 h, and (c) 336 h.

controlled at a certain level of low temperature(196 °C). Along with the continuous generation of the high frequency induction, the metal will continuously be vaporized, condensed and stored at the surface of the collector. High frequency induction heating system can steadily and continuously heat the material, and the pressure and temperature inside the vacuum chamber can easily be controlled under the ideal conditions. Therefore, the acquired powdery particles can evenly be nucleated and grow, acquiring nanoscale metal particles. Since the material is collected and stored on the collection surface of the collector inside the vacuum chamber by means of vaporization and condensation, particles can rapidly be acquired, which is an excellent method of mass production of nanoparticles.

3. RESULTS AND DISCUSSION

This research uses zinc bulk to produce ZnO nanoparticles by means of high frequency induction heating vaporization and gas condensation method. The major focus of the research rests upon the adoption of a very low-temperature liquid nitrogen condensation collector, as well as the successful development of an automatic nanoparticle collection system. This system not only can collect nanoparticles that are just condensed, but also avoid such phenomenon as aggregation and growth *etc*. of the nanoparticles during the collection process due to over-accumulation.

During the process of vaporization, owing to the gas convection, the vaporized smog will rapidly loss its energy and condenses into nanoparticles due to its collision with the atoms of inert-gas. Along with the He, the nanoparticles will then rush rapidly towards the surface of the very low-temperature collector, which then condense and form into nanoparticles. Under the criteria of a lower pressure and lower collection temperature, the growth of nanoparticles is constrained. During the collection process, liquid nitrogen is continuously injected into the collector to maintain a processing temperature at –196 °C, as well as working pressure at 10 Torr. Besides, the working inert-gas is He and the collection distance is 25 mm, enabling the collection surface of the collector to maintain at a low temperature stably. Upon FE-SEM measurement, the result of the acquired nanoparticle is shown in Fig. 2. All the nanoparticles are in the structure of a hexagonal prism and its average particle size is 20 nm. Fig. 2 shows that the size of the ZnO nanoparticle is very consistent.

Based on a fixed proportion, the nanoparticles are placed inside the deionized water for 72 h, 168 h, and 336 h respectively, so as to observe the oxidation and precipitation status of the nanoparticles. In order to verify that the

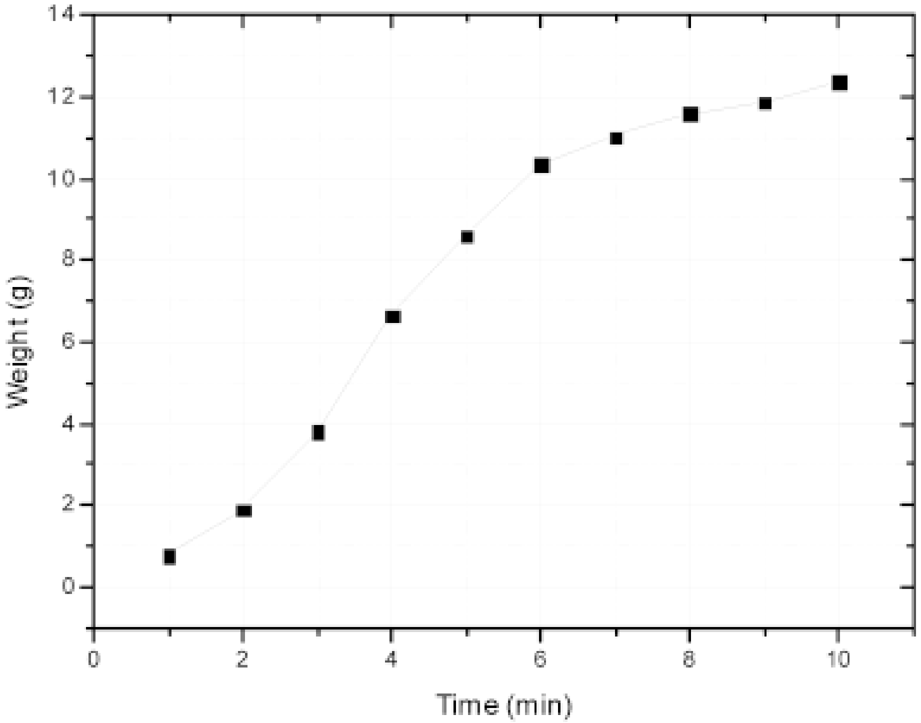
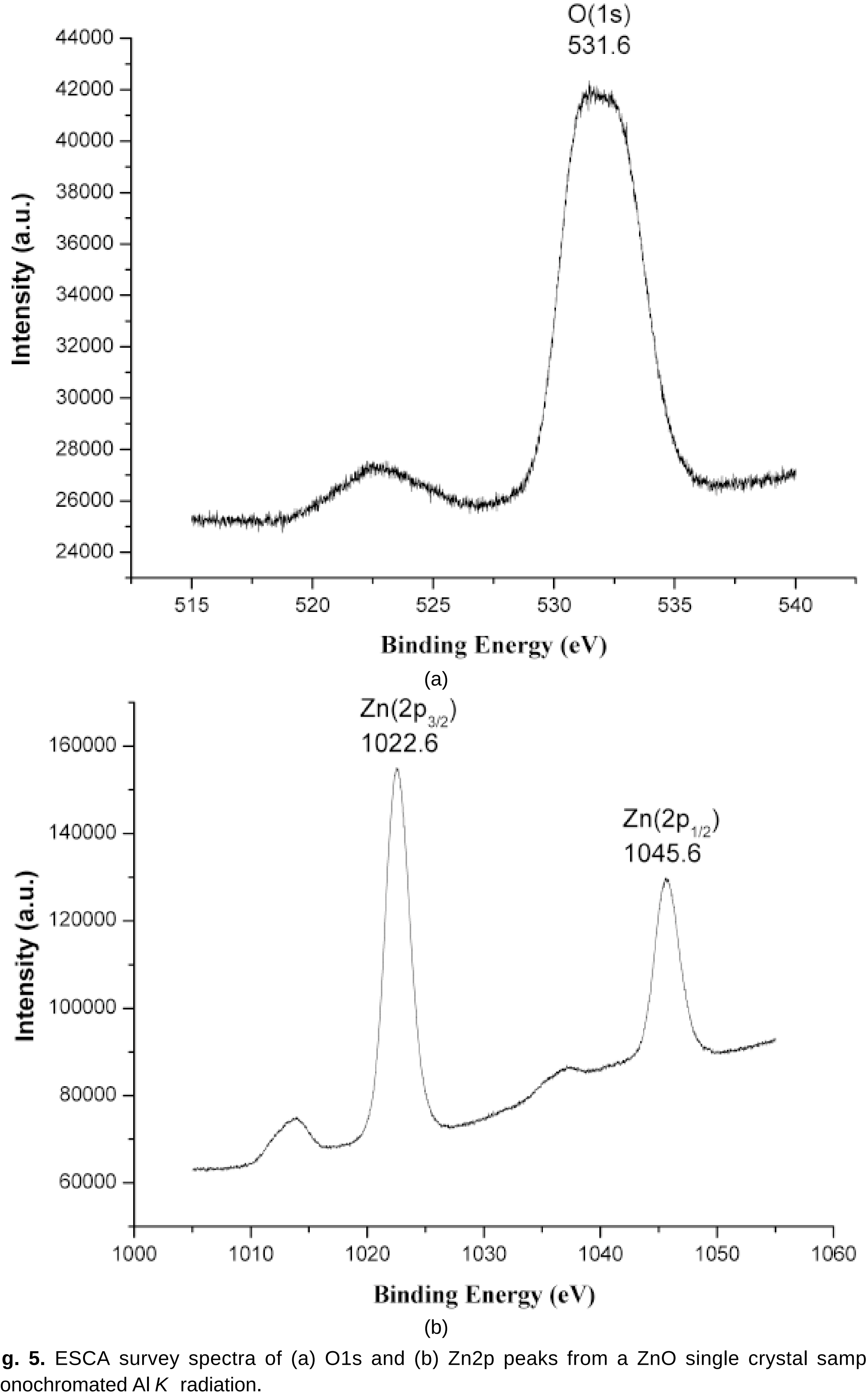


Fig. 4. Weight of the nanoparticles collected in the collector at different time segment.

nanoparticles inside the deionized water will change along with the passing of time, researchers adopt FE-SEM image to observe the nanofluid. Fig. 3a is the FE-SEM image of ZnO nanofluid after placement of 72 h. From this image, it is clearly judged that the particle is in ZnO nanostructure. However, this research uses physical method to produce nanoparticles, and dispersant is not used to undergo dispersion treatment towards the nanofluid, therefore it can clearly be checked from this figure that ZnO has started to grow but still maintained at a regular shape of hexagonal prism. Its axial length is around 250 nm. Fig. 3b shows the FE-SEM image of the same nanofluid after placement of 168 h. Although the former shape of the nanoparticle can still be identified, it can be clearly observed that it has grown into a hexagonal prism of around 500 nm. Fig. 3c shows the FE-SEM image of the same nanofluid after placement of 336 h. It can be clearly seen that the nanoparticles do not have a fixed shape and their distribution is not obvious, but in turn, they become oxidized material clustering and growing irregularly.

Put the zinc bulk of weight 52 gram under 10 Torr of vacuum pressure to vaporize. The preset heating temperature is 595 °C and the collection distance is 25 nm. During the vaporization processing, Helium gas is used for condensation and automatic nanoparticle collection system of liquefied He condensation is used to collect the ZnO nanoparticles. Based on these parameters, the weight of the collected nanoparticle is calculated at every collection time segment. It is known from Fig. 4 that during the collection time between 1~6 minutes, the speed of collecting the nanoparticle is faster, acknowledging that the vaporization process tends to proceed during this time segment. During the collection time of 7 ~ 10 minutes, the collection speed of nanoparticles tends to slow down relatively.

From this experiment, we can judge that during the process of material that starts to vaporize, the collection speed of nanoparticles is not consistent. Therefore when controlling the automatic collection system, we should make proper adjustment based on this characteristic. Within the time range of 1 ~ 6 minutes when the metal starts to vaporize, we should set the scraper rotational speed at 1/12 rps. Within the range of 7 ~ 10 minutes, it should be set at 1/16 rps, maintaining a consistent collection rate of the nanoparticles.



(a)

(b)

Fig. 5. ESCA survey spectra of (a) O1s and (b) Zn2p peaks from a ZnO single crystal sample. Monochromated Al K_α radiation.

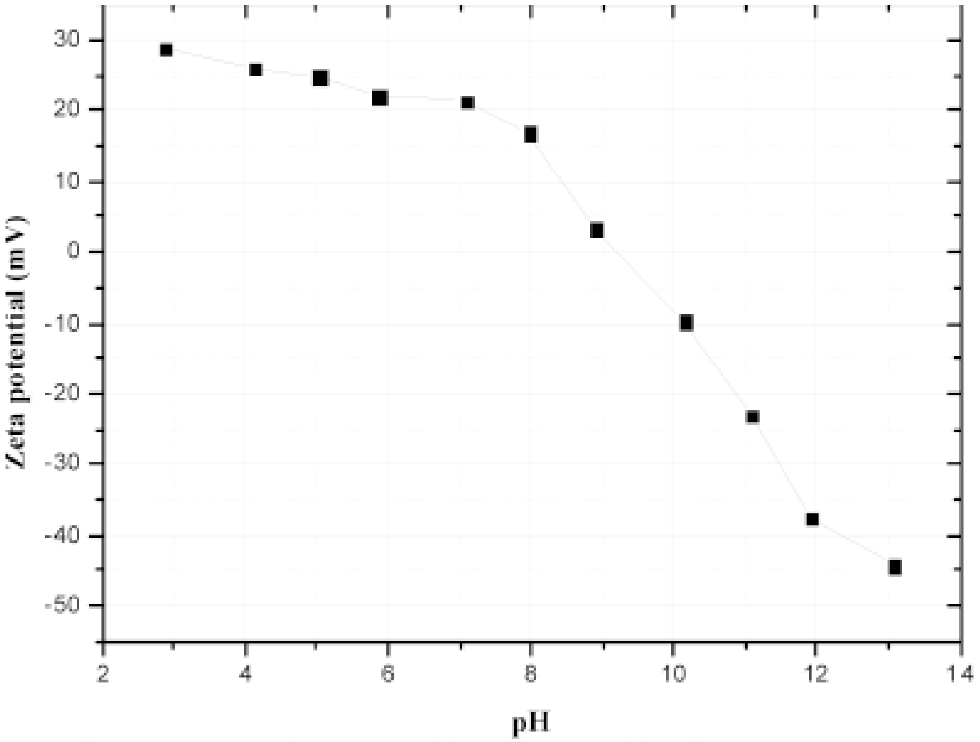


Fig. 6. Zeta potential measured by ZnO nanofluid at different pH values.

The XRD pattern indicates formation of ZnO crystals, which can be confirmed by the ESCA measurement. A full-range scanning reveals the types of elements contained in the sample. When chemical shift scanning is applied to different elements, the chemical environment and state of single element can further be acquired. As shown in Fig. 5a, after the oxygen of the sample undergoes chemical shift scanning, a signal occurs at the binding energy of 531.2 eV. According to the handbook of X-ray photoelectron spectroscopy [11], the binding energy of the O 1s is 529.9 eV, implying that the fabricated nanoparticle is oxide. Secondly, upon chemical shift scanning of Ti, as shown in Fig. 5b, two signals occur at the binding energy of 1022.8 eV and 1045.9 eV respectively. According to the handbook of X-ray photoelectron spectroscopy, the binding energy of the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of ZnO are 1022 eV and 1045 eV respectively. Therefore, the fabricated nanoparticle is confirmed to be TiO_2. The spectrum is in good agreement with the standard spectrum of ZnO. All the binding energies are referenced to C 1s at 284.5 eV.

Zeta potential is an important parameter that reflects the behavior of colloid. By the ZnO nanoparticles produced by the equipment developed in this research, nanofluid with concentration of 0.05 wt.% can be allotted. When the Zeta potential of the ZnO nanofluid is zero, the surface of the particle does not carry electric charge. Under this condition, the phenomenon of condensation is easy to occur towards the suspension particles. When the density of the electric charge on the surface of the particles is higher, the particles carry a higher Zeta potential. The high density of the electric discharge on the surface of the particles can make a larger repulsive force of the static electricity between the particles. This force can make the nanofluid to maintain a higher stability. By adjusting the pH value of the nanofluid, a certain amount of surface electric charge can be produced on the surface of the nanoparticles, forming double electric layers. The repulsive force between the double electric laters force offsets the mutual attraction between the particles and this mechanism is beneficial to the dispersion of the suspension particles. Before measuring the Zeta potential, 10^{-1} M of hydrochloric acid and NaOH is used to mix with deionized water so as to come up with ZnO nanofluid having different pH value. Figure 6 shows the mea-

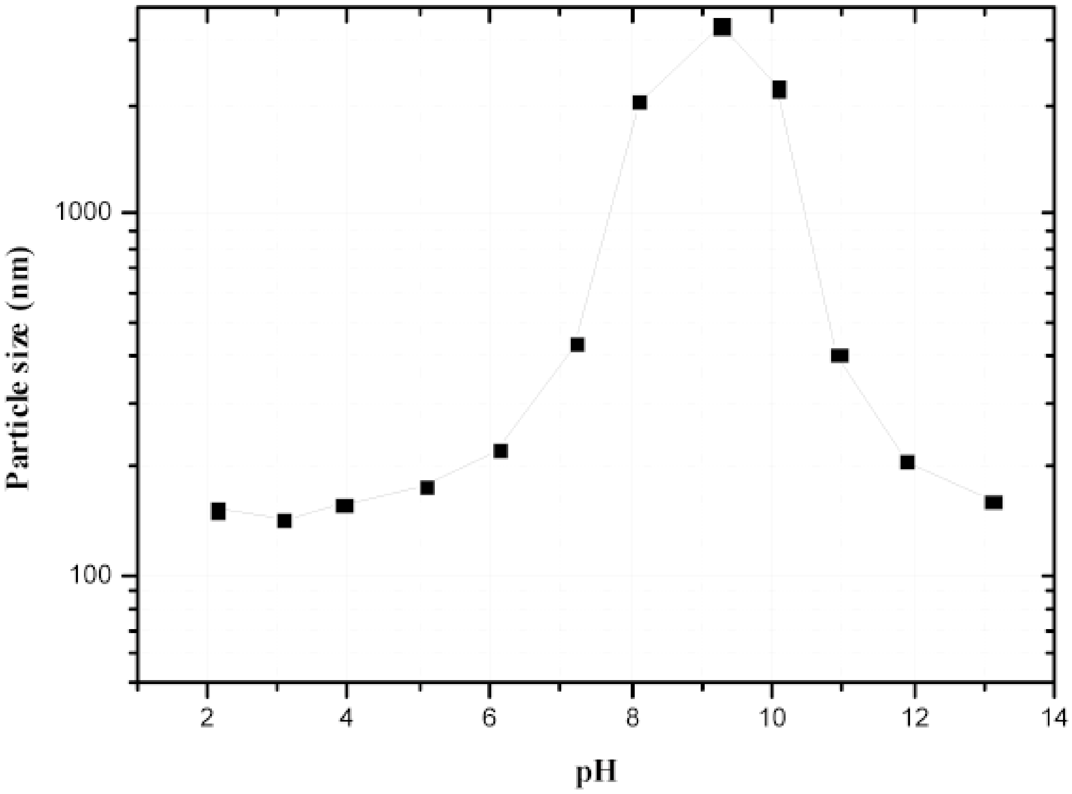


Fig. 7. The measured mean secondary particle size of the ZnO nanofluid having different pH values.

sured Zeta potential of ZnO nanofluid having different pH value. Fig. 7 shows the measured mean secondary particle size of the nanofluid having different pH value. By comparing Fig. 6 and Fig. 7, it is known that the mean secondary particle size of the ZnO nanofluid on the isoelectric point is the largest. When the pH value is larger than 9.27, the surface of the particles carry negative electricity. When the pH value is smaller than 9.27, the surface of the particles carry positive electricity. Therefore, because of a smaller Zeta potential, phenomenon of clustering occurs in the particles having their pH values between 7 ~ 11, making an obvious increase of the mean secondary particle size. It is because the repulsive force between the surface double electric layers cannot resist the mutual attractive action between the particles, so that suspension particles having stable dimension cannot be acquired [12,13].

Upon the illumination of light, ZnO nanofluid can transform the photoenergy into chemical energy, so as to enable the synthesis or the decomposition of the organic materials. Because of its remarkable oxidation reduction capability, high chemical stability and poisonless characteristics, it is most commonly applied in pollutants removal and disinfectants. When the ZnO is shone under ultra-violet light of wavelength less than 400 nm, the electrons of the valence band will be excited by the energy of the ultra-violet ray and jump to conduction band, and at the same time, the valence band will create electric holes carrying positive electricity. Since the holes will react with the absorbed O^- or H_2O to create OH free radicals, which can further generate the actions such as disinfection or deodorization. Fig. 8 is the measured UV-Vis absorption spectra of ZnO nanofluids fabricated by this system. It can clearly understand from this figure that the ZnO nanofluid fabricated by this system carries light absorption ability at the wavelength of 350 nm. And when the wavelength is at the range of 350 nm to 550 nm of UV-Vis, the energy will all be absorbed by the ZnO particles inside the nanofluid. At this moment, the electrons receive enough energy to excite from valence band to conduction band.

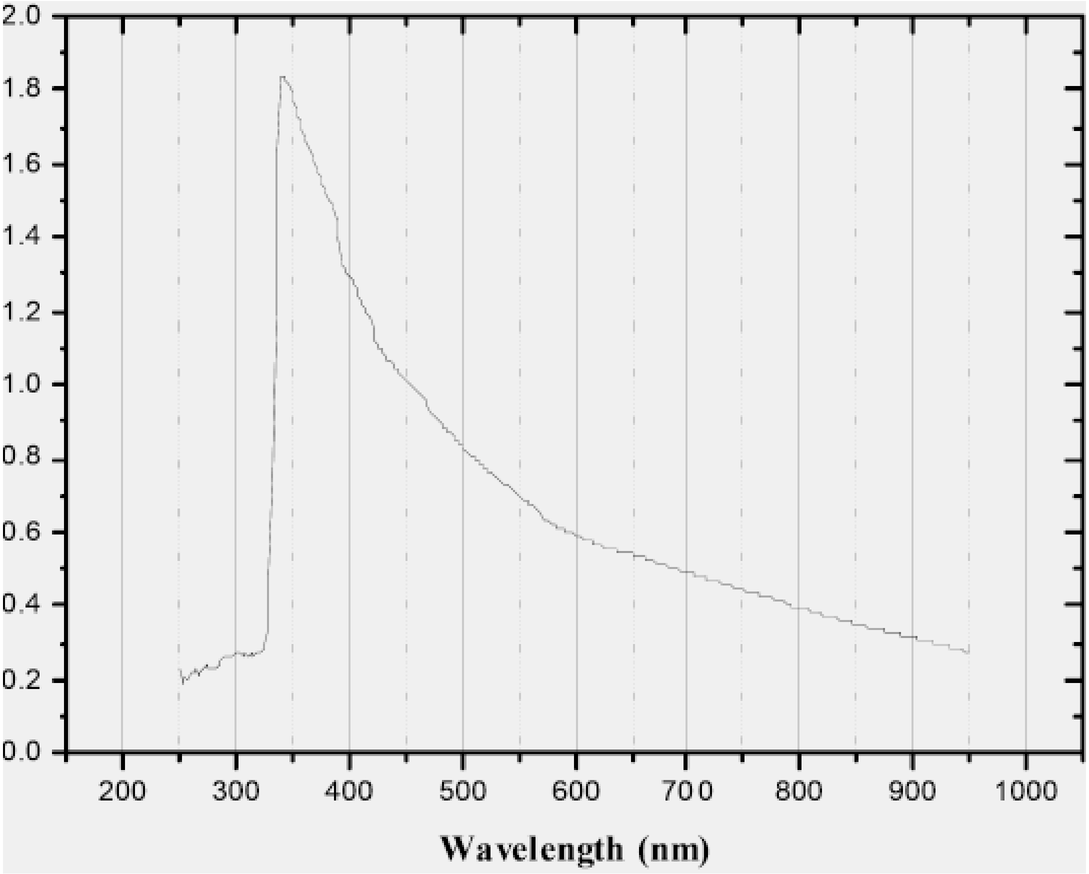


Fig. 8. UV-Vis absorption spectra of ZnO nanofluids.

4. CONCLUSIONS

The innovative nanoparticle synthesis system developed in this research applies to the theory of gas condensation method to produce ZnO nanoparticles. Experiment result shows that by the high frequency gas condensation method developed in this research to undergo nanoparticle synthesis, as well as the adoption of automatic collection system of liquid nitrogen condensation, ZnO nanoparticles of pure quality can be directly produced. Besides, a monitor system having USB transmission and an illumination system are installed inside the vacuum chamber, so as to monitor the synthesis process of the nanoparticles inside the vacuum chamber. The properties of the produced nanoparticle suspension have been identified by the FE-SEM, Particle-Size Analyzer, Zeta potential, ESCA, UV-Vis. and spectrophotometer. From the experimental results and the discussion above, the following conclusions are made.

1. The nanoparticles produced by this system is allotted into nanofluid by 0.05% weight percentage. Upon still placement of 72 hours, phenomenon of oxidization occurs, forming nanoparticles in the shape of hexagonal prism. After 168 hours, it grows into the shape of square-hexagonal prism of size around 500 nm.
2. ESCA is used to confirm the chemical element compositions and form of the ZnO nanoparticle fabricated by this system. It is confirmed that the powder produced by this system is really ZnO.
3. When the Zeta potential is 0, the pH value of ZnO nanofluid is 9.27. So when the pH is larger than 9.27, the surface of the particle carries negative electricity, whereas when it is smaller than 9.27, it carries positive electricity. When the pH value lies between 7 to 11, phenomenon of clustering occurs towards the particles because the Zeta potential is too smaller, making the

mean secondary particle size increases obviously.

4. Within the wavelength range of 350 nm to 550 nm of UV/Vis, the energy absorbed by the ZnO particles inside the suspension fluid.

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